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International Classification :—B 24 d (C 08 j).

COMPLETE SPECIFICATION.

Foamed Shaped Bodies Containing a Polyvinyl Acetal for Use in Grinding or Polishing.

We, KALLE AKTIENGESELLSCHAFT, a Body Corporate organised according to the laws of Germany, of 190—196 Rheingaustrasse, Wiesbaden-Biebrich, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with foamed shaped bodies containing a polyvinyl acetal for use in grinding or polishing.

Known polishing bodies based on organic material include such as contain plastics or rubber as binder for the abrasive ingredients. The foamed plastic and sponge-like bodies with a content of abrasives which are described in the literature belong to this type of bodies. These products are not fully satisfactory. Thus, polishing bodies made of plastics are generally very hard, rigid and brittle. Although certain kinds have some advantages, they are easily clogged and have a tendency to smear. Experience has shown that polishing bodies containing rubber as a binder begin to smear when the heat generated during the polishing process becomes too high. Consequently, only thin polishing discs of this kind are used in practice. Their hardness is not very vari-

able and, moreover, it is not possible to introduce a relatively high proportion of abrasives into rubber grinding wheels. A further disadvantage of the polishing bodies of this kind is that several working steps, such as compression, hardening, and vulcanization, are required for their preparation.

The foamed plastic and sponge-like polishing discs recently described in the literature are, above all, unsatisfactory as regards resistance to abrasion and breaking. As their content (by volume) of abrasives is relatively low, they are not very effective and rapidly wear away. Very often, expensive organic solvents or softeners must be used in and a number of working steps are required for the preparation of the finished shaped bodies.

The present invention provides a process for the manufacture of a foamed shaped body containing a polyvinyl acetal for use in grinding or polishing, which comprises foaming an aqueous reaction mixture comprising in solution a vinyl alcohol polymer having a hydroxy content equivalent to an average degree of hydrolysis of at least 80%, formaldehyde and an acid catalyst, together with a finely divided water-insoluble thermoplastic resin material and an abrasive, by

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beating air into the mixture, setting the resulting foam in a mould, and washing and drying the moulded shaped body, the amount of aldehyde being such as to bring the percentage of reacted hydroxyl groups in the polyvinyl alcohol up to 30 to 85%.

The new porous, elastic, shaped bodies can be further processed to form polishing bodies. Said shaped bodies as far as their properties are concerned, stand between the polishing bodies based on non-foamed plastic materials and those based on foamed plastics.

By the process of the invention the result is achieved that the abrasives are embedded into a mixed binding material. When the reaction is completed, this mixed binder consists of polyvinyl formal, with or without a content of another polyvinyl acetal or a polyvinyl ketal or a mixture thereof, into which the plastic resin material is incorporated or in which it may even be combined chemically. The capacity of this mixed binder as matrix for abrasives is very high, and it is determined mainly by the content of the thermoplastic resin material, which may be natural or synthetic. The shaped bodies are more or less porous and the finished foamed products are of great strength. A maximum polishing capacity of shaped bodies cut from the moulded material can be obtained by selecting mixtures with the optimum proportions of constituents. The most suitable proportion of the thermoplastic resin material present varies according to its nature.

The expression "abrasives" as used in the present Application is meant to designate the substances customarily used for the preparation of polishing and grinding agents and includes such materials as: corundum, silicon carbide, boron carbide, emery, pumice, glass powder, quartz, tripoli, chalk, oxides of chromium, iron, cerium and beryllium, and diamond dust. The grain size may be selected according to the purpose for which the finished article is to be used. Mixtures of different abrasives and different grain sizes may also be used.

For special effects, filling materials of all kinds may be added, in addition to the above stated polishing materials, to the polyvinyl alcohol solutions used in the process of the present invention, in particular filling materials of fibrous structure, e.g. natural or synthetic fibres.

The thermoplastic resin materials to be added to the polyvinyl alcohol solutions in accordance with the present invention are predominantly added in the form of dispersions or as a powder. They must be compatible with polyvinyl alcohol and with the other substances present. Suitable substances to be added in a dispersed state are, for example, polyvinyl esters and polyacrylic

esters and their copolymers, polyacrylates, polymethacrylates, polyacrylamides, polyvinyl ethers, polyisobutylene, polystyrene, polyvinyl chloride, and polyvinylidene chloride and their copolymers, copolymers of butadiene-styrene or butadiene-acrylonitrile. All dispersions are suitable that are sufficiently compatible with the other substances present in the solution. The average grain size of the solids contained in the polymer dispersions should range from 0.01μ to 10μ . This high degree of distribution not only causes an increase of the binding capacities of the material which permits a considerable reduction of the content of binders, but also gives rise to a higher chemical reactivity of the substances.

Thermoplastic resin materials that do not impede the foaming power of the reaction mass may be added to the polyvinyl alcohol solutions in pulverized form. Suitable compounds of this type are: polyethylene, polypropylene, polyamides, shellac, colophony, colophony-modified phenol formaldehyde condensates, coumarone resins, modified coumarone resins, chlorosulphonated polyethylene, terephthalic acid polyesters, polycarbonates, and the materials listed above as being suitable for addition in a dispersed state. The powder particles should advantageously have a diameter of less than 0.1 mm., which can be achieved by a suitable treatment. If added in pulverized form, the thermoplastic resin materials are less effective than their dispersions, i.e. a greater quantity of binder is necessary per kilogram of abrasive.

Mixtures of binders in dispersed or pulverized form may also be added to the polyvinyl alcohol solutions, the results obtained often being of particular advantage.

Thermoplastic resin materials which are capable of reaction with formaldehyde as well as with polyvinyl alcohol, or which can be partially modified in chemical respects by another substance present in the reaction mixture are preferably used. Polyvinyl esters, for instance, which are partially saponified, can be easily cross-linked with polyvinyl alcohol by means of formaldehyde. Polyamides, colophony, and polyacrylamides may be introduced by the same method. This solidifying process of the reaction mixture, which is a partly chemical, partly physical reaction, yields binding materials which, as supporting materials for the abrasives, possess particular advantages which the single binding components do not have. The thermoplastic properties of this new combined binding material permit greater quantities of abrasives to be included and thus favourably affect the grinding process. If small quantities of sulphur, a vulcanizing accelerator and zinc oxide are added to compositions which contain vulcan-

beating air into the mixture, setting the resulting foam in a mould, and washing and drying the moulded shaped body, the amount of aldehyde being such as to bring the percentage of reacted hydroxyl groups in the polyvinyl alcohol up to 30 to 85%.

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izable compounds, the finished discs can be after-vulcanized at temperatures ranging from 125 to 160° C., thus producing discs resembling hard rubber.

5 It is a further advantage of the process according to the present invention that the porosity of the products to be produced can be varied by selecting a mixture of suitable proportions or varying the conditions 10 of the process. It is possible to produce pores of a size which is many times that of the abrasive particles present. A thorough cooling during the polishing process follows from this high porosity. Moreover, the products of the present invention have the advantage that, due to the plasticity of the binding material, a coarse grain used in the 15 polishing body according to the present invention has the same effect as a considerably finer grain used with other grinding and 20 polishing bodies. With the products of the present invention, the effect of the same size of grain is somewhat mollified. Because abrasives of a finer granulation are much 25 more expensive, this fact alone is of considerable advantage from the point of view of economy.

The kind of bond formed and, hence, the 30 hardness of the grinding and polishing tools prepared from the shaped bodies can be varied within a wide range by selecting suitable proportions of the components used, i.e. polyvinyl alcohol and thermoplastic resin material. The proportions may vary 35 from a ratio of 0.5:1 to a ratio of 25:1, the preferred ratios being from 0.9:1 to 8:1, based on the weight of the solid products.

Further, it has been found that besides 40 the beforementioned plastics, there may be embodied into the mass for making the polishing bodies water-soluble resins which are capable of reacting with formaldehyde under the reaction conditions prevailing in the present process. Products of this kind 45 are particularly suitable for the production of stones for cleaning kitchen ranges.

In order to achieve an especial cooling 50 effect with the grinding and polishing bodies according to the present invention, customary grinding and polishing pastes and/or pulverized paraffin may be added to the polyvinyl alcohol composition. The essential feature of the invention is, however, that by using a finely divided thermoplastic 55 resin material as an addition to the polyvinyl alcohol which is then converted into a polyvinyl acetal, a porous structure is produced which is capable of binding a high percentage of abrasive. This porous structure is of a sponge-like nature and permits the access of air to all parts of the finished body. The strength of the cell walls which are formed and consist of organic compounds is the better the lower the degree 60 of foaming.

All types of polyvinyl alcohol of low, medium, or high viscosity, in which the hydrolizable fractions are hydrolyzed to at least 80%, can be used in the process according to the present invention. Suitable polyvinyl alcohol products are, e.g. the products commercially available under the Trade Names "Moviol" and "Polyviol". Less than 20% of the hydroxyl groups may be initially transformed into acetals provided that the compounds are still water-soluble. Copolymers and/or graft polymers of vinyl alcohol, in admixture with polyvinyl alcohol, may also be used. Such substances are, for example, copolymers of a vinyl ester with another monomeric vinyl compound, which copolymer is subsequently saponified, or a graft polymer obtained by hydroxyalkylation or cyanoethylation. The grinding and polishing tools prepared with these compositions are of particular advantage.

After the reaction of the aldehyde present with the polyvinyl alcohol is completed, 30 to 85% of the hydroxyl groups should be transformed into acetals or otherwise chemically bound.

For acceleration of the reaction, in particular of the formation of the acetal, strong or weak mineral or organic acids are added to the reaction mixture, e.g. acetic acid, formic acid, oxalic acid, or para-toluene sulphonic acid, in concentrations ranging from 2—70%. The formaldehyde component is preferably added in the form of a 30—40% aqueous solution. Other mono-, di-, or trialdehydes which do not disturb the foaming process may also be introduced into the reaction mixture containing formaldehyde and polyvinyl alcohol. Compounds which under the reaction conditions of the present process split off formaldehyde or another aldehyde, e.g. polymeric formaldehyde or polyacroleins, may also be used in the present process. A considerable acceleration of the coagulation may be achieved by adding bases containing nitrogen, such as amines, urea, guanidine derivatives and their condensation resins. The addition of 1—8% of glutaric dialdehyde has the same accelerating effect. Part of the aldehyde may analogously be replaced by a ketone, advantageously applying a somewhat higher reaction temperature.

The process of the present invention is illustrated by the following description:—

Formaldehyde is caused to begin to react with a polyvinyl alcohol in an aqueous solution, in the presence of a mineral acid and of a thermoplastic resin material, which may be added in the form of a powder, or, even more advantageously, as an aqueous dispersion. If desired, also a surface-active agent may be present in the solution. To this reaction mixture, abrasives of different types and of the desired grain size are then

added. During the reaction, larger or smaller quantities of air are introduced by agitating. The foam thus produced is poured into moulds and allowed to coagulate at temperatures ranging from 20 to 100° C. Within 2 to 120 hours, the reaction mixture accepts the shape given to it. Any shape may be given to the foam material. However, it is preferably poured into cylindrical moulds to form cylindrical shaped bodies which are subsequently cut into discs. The shaped body is then washed and dried at temperatures ranging from 30 to 70° C. A further hardening of the material can be achieved by a prolonged heating, advantageously with the exclusion of air, to temperatures which range from 120 to 150° C. Within this temperature range, the polyvinyl formal splits off water so that ethylene bonds are formed in the molecule, which cause an additional solidification of the material. In addition thereto, further cross-linking reactions are initiated.

The reaction process is brought to an end by neutralizing the reaction mixture. For this purpose, ammonia is preferably used, because it is also capable of binding the aldehyde component.

In the process according to the present invention the abrasives are evenly distributed and bound. The material obtained may be compressed with heating and thus further hardened at the expense of its elasticity.

The technical progress of the present invention resides in the fact that, in one process step, shaped bodies are obtained which contain abrasives and which can be made into finished grinding and polishing discs by a simple cutting or shaping process. The shaped bodies of the present invention are distinguished by their high elasticity and grinding power and by their resistance to abrasion and breaking. The polishing discs thus obtained have an open structure and can be used with excellent results for dry grinding or polishing and for profile grinding purposes. Even at higher grinding temperatures no clogging of the pores could be detected. The new polishing discs do not have the before-mentioned drawbacks, or they are at least markedly reduced.

The following examples illustrate the invention; in the examples foaming is performed by beating air into the mixture:—

EXAMPLE 1.

To an aqueous solution containing 216 grams of polyvinyl alcohol there are added 350 ml. of 30% formalin, 560 grams of an aqueous polyvinyl acetate dispersion, 410 ml. of a 16.8% hydrochloric acid, and 3.6 kg. of corundum having a grain size of 60. The mass is intimately mixed and then foamed until the foam has reached a volume

of 5.9 litres. In the course of the foaming-up operation, the polyvinyl acetate is saponified, at least 10% of the ester groups remaining unsaponified. At room temperature, the mixture is poured into moulds and kept standing for 2 to 6 days. Very hard discs are obtained.

EXAMPLE 2.

The procedure described in Example 1 is repeated using a mixture of 294 grams of polyvinyl alcohol (in aqueous solution), 425 ml. of formalin, 500 grams of an aqueous dispersion of polyvinyl propionate, 3.37 kg. of highly purified corundum having a grain size of 220, and 225 ml. of 54% sulphuric acid. When the mass was poured into the moulds, the foam had a volume of 5 litres.

EXAMPLE 3.

A mixture consisting of 47.5 grams of polyvinyl alcohol and 47.5 grams of a polyvinyl alcohol having 4% of butyral groups, is foamed in an aqueous solution with 90 ml. of 30% formalin, 30 ml. of 30% glyoxal solution, 130 ml. of 22% hydrochloric acid, 219 grams of a 40% aqueous dispersion of a styrene-butadiene copolymer, and 1.72 kg. of silicon carbide, until a foam volume of 3 litres is obtained.

EXAMPLE 4.

A mixture made up from 157 grams of polyvinyl alcohol, 210 ml. of 30% formalin, 2.8 kg. of glass powder of a grain size of 100, 112 ml. of concentrated hydrochloric acid, 415 grams of an aqueous polyvinyl acetate dispersion, and 415 grams of an aqueous polyvinyl propionate dispersion, the polyvinyl alcohol being in aqueous solution, is foamed until 5 litres of foam are obtained and then poured into moulds.

EXAMPLE 5.

To an aqueous solution of 66 grams of polyvinyl alcohol there are added 30 grams of pulverized polypropylene, 91 ml. of 30% formaldehyde, 60 ml. of concentrated hydrochloric acid, 20 grams of an aqueous dispersion of an acryl ethyl ether polymer, and 600 grams of silicon carbide having a grain size of 150. After intimately mixing the components, the mixture is foamed until it has reached a volume of 1 litre and then poured into a mould. When the mass has solidified, it is washed, dried and cut into discs which can be used as polishing wheels.

EXAMPLE 6.

A mixture made up from 256 grams of polyvinyl alcohol, 405 ml. of 30% formaldehyde, 225 ml. of 42% sulphuric acid, 10 ml. of a wetting agent, 200 grams of an aqueous polyvinyl chloride dispersion, 200 grams of an aqueous polyvinyl isobutyl

added. During the reaction, larger or smaller quantities of air are introduced by agitating. The foam thus produced is poured into moulds and allowed to coagulate at temperatures ranging from 20 to 100° C. Within 2 to 120 hours, the reaction mixture accepts the shape given to it. Any shape may be given to the foam material. However, it is preferably poured into cylindrical moulds to form cylindrical shaped bodies which are subsequently cut into discs. The shaped body is then washed and dried at temperatures ranging from 30 to 70° C. A further hardening of the material can be achieved by a prolonged heating, advantageously with the exclusion of air, to temperatures which range from 120 to 150° C. Within this temperature range, the polyvinyl formal splits off water so that ethylene bonds are formed in the molecule, which cause an additional solidification of the material. In addition thereto, further cross-linking reactions are initiated.

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of 5.9 litres. In the course of the foaming-up operation, the polyvinyl acetate is saponified, at least 10% of the ester groups remaining unsaponified. At room temperature, the mixture is poured into moulds and kept standing for 2 to 6 days. Very hard discs are obtained.

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A mixture consisting of 47.5 grams of polyvinyl alcohol and 47.5 grams of a polyvinyl alcohol having 4% of butyral groups, is foamed in an aqueous solution with 90 ml. of 30% formalin, 30 ml. of 30% glyoxal solution, 130 ml. of 22% hydrochloric acid, 219 grams of a 40% aqueous dispersion of a styrene-butadiene copolymer, and 1.72 kg. of silicon carbide, until a foam volume of 3 litres is obtained.

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EXAMPLE 6.

A mixture made up from 256 grams of polyvinyl alcohol, 405 ml. of 30% formaldehyde, 225 ml. of 42% sulphuric acid, 10 ml. of a wetting agent, 200 grams of an aqueous polyvinyl chloride dispersion, 200 grams of an aqueous polyvinyl isobutyl

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ether dispersion, 1.3 kg. of corundum of a grain size of 240, and 1.2 kg. of pumice powder, the polyvinyl alcohol being in aqueous solution, is foamed until it has a volume of 4.9 litres.

EXAMPLE 7.

A mixture made up from 106 grams of polyvinyl alcohol (graft polymer), 220 ml. of 30% formaldehyde, 300 grams of an aqueous polymethacrylate dispersion, 170 ml. of a 25% hydrochloric acid, and 1.35 kg. of corundum having a grain size of 60, dispersed in water, the polyvinyl alcohol being in aqueous solution, is foamed until it has a volume of 3.1 litres. The foamed mass is poured into moulds and kept standing for 3 days.

EXAMPLE 8.

169 grams of polyvinyl alcohol, 340 ml. of 30% formaldehyde, 200 ml. of 22% phosphoric acid, 10 ml. of a wetting agent, being a 1% solution of fatty alcohol sulphonate, 250 grams of an aqueous polyisobutylene dispersion, 250 grams of an aqueous polyvinylidene chloride dispersion, and 1.7 kg. of emery of the granulation 2/0 are intimately mixed, and the mixture, in which the polyvinyl alcohol is in aqueous solution, is foamed to a volume of 5 litres, and then poured into a mould.

EXAMPLE 9.

310 grams of polyvinyl alcohol, 470 ml. of 30% formaldehyde, 220 ml. of 45% sulphuric acid, 140 grams of an aqueous polystyrene dispersion, 30 grams of an aqueous polyvinyl isobutyl ether dispersion, and 700 grams of chromium oxide are intimately mixed in 0.9 litre of water and the mixture, in which the polyvinyl alcohol is in aqueous solution, is then foamed to a volume of 4.3 litres. The foam is poured into moulds and kept standing for 2 days at a temperature of 55° C.

EXAMPLE 10.

45 87 grams of polyvinyl alcohol, 178 ml. of 30% formaldehyde, 100 ml. of hydrochloric acid, 1.75 kg. of glass powder having a grain size of 80, 100 grams of an aqueous polyvinyl isobutyl ether dispersion and 200 50 grams of a water-soluble phenol aldehyde resin which is still miscible with water, are intimately mixed and the mixture, in which the polyvinyl alcohol is in aqueous solution, is then foamed to a volume of 2.4 litres. 55 The products thus obtained are very suitable for use as stones for cleaning kitchen ranges.

EXAMPLE 11.

60 125 grams of polyvinyl alcohol which is to 30% cyano-ethylated, are dissolved in water and then intimately mixed with 139 ml. of 30% formaldehyde, 27 grams of an

aqueous butadiene-acrylonitrile dispersion, 108 ml. of a 22% hydrochloric acid, 625 grams of silicone carbide of a grain size of 180, and 50 grams of pumice powder. The mixture is foamed to a volume of 2 litres, poured into moulds and then kept standing at 65° C. After one day the solidified sponge-like mass can be cut to 70 very dense polishing discs.

EXAMPLE 12.

125 grams of polyvinyl alcohol, 142 ml. of 30% formaldehyde, 100 grams of an aqueous butadiene-styrene dispersion, 42 75 grams of a polystyrene dispersion, 142 ml. of 50% sulphuric acid, 1.3 kg. of corundum of a grain size of 60, and 0.3 kg. of very fine pumice powder are intimately mixed. The mixture, in which the polyvinyl alcohol is in aqueous solution, is foamed in known manner to a volume of 3 litres. After the foam mass has been poured into moulds and kept standing for 4 days, a product was obtained which was very hard and, when used in the form of discs, proved to be very effective for polishing purposes.

EXAMPLE 13.

An aqueous mixture containing 232 grams of polyvinyl alcohol in solution, 17 ml. of a wetting agent, being a 1% solution of fatty alcohol sulphonate, 425 ml. of 30% formaldehyde, 200 grams of shellac powder, 189 ml. of 50% sulphuric acid, and 8 kg. of glass powder of a grain size of 60, is foamed to a volume of 5 litres and then poured into moulds. Discs cut from the mass after solidification are excellently suited for the processing of wood.

EXAMPLE 14.

An aqueous mixture of 342 grams of polyvinyl alcohol (in solution), 420 ml. of formalin, 179 ml. of hydrochloric acid, 1.3 kg. of glass powder having a grain size of 200, and 200 grams of a pulverized polyvinyl chloride containing 13% of maleic acid in the polymer, is foamed in known manner with 35 grams of polyacrylonitrile fibres having a titre of 10 denier and a length of 10—30 mm. until a volume of 5 litres is 110 obtained. After the foamed mass has been poured into moulds and kept standing for 2 days at a temperature of 50° C. in order to cause coagulation it is washed with water to remove the acid and dried. A porous 115 product is thus obtained.

EXAMPLE 15.

A grinding body produced in accordance with Example 5 is, in a dry state, heated for a short time to 160—170° C. and then 120 pressed in a mould in such a way that the original volume is reduced by 40%. The compressed bodies obtained are suitable for

grinding steel, aluminium, brass, grey pig iron and plastics.

hydroxyl groups in the polyvinyl alcohol up to 30 to 85%.

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2. A process as claimed in Claim 1, in which, after washing and drying, the moulded body is heated and compressed with reduction of the volume.

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3. A process for the manufacture of a shaped body as claimed in Claim 1, conducted substantially as described in any one of the examples herein.

4. A foamed shaped body, when made by the process claimed in any one of Claims 1—3.

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